SCIENCE

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*PROGRESS IN PHYSICAL CHEMISTRY.**

IN these days of far-reaching specialization the would-be speaker upon any subject is between a new Scylla and a new Charybdis. In order that his production should be comprehensible to those outside of the specialty it must almost inevitably be made boresome to those within the fold; but, on the other hand, that which is new to the specialist in his own topic is apt to be quite too new to the layman. Either popularizing or specializing is likely to wreck the speaker's purpose by inducing at least a part of his audience to slumber; and this danger is especially imminent after dinner on a hot day which has been filled with mental effort. In this brief address, which Professor Smith has entrusted to my care, I shall probably run foul of both obstructions; but this irregular course will have the great concomitant advantage of permitting each class of hearers to obtain a few minutes of much needed repose.

We are rather accustomed to look upon physical chemistry as being a very modern invention, and in one sense we are not wrong in so doing. But after all, many of the fundamental generalizations of physical chemistry are by no means recent, and some of them are really old. Leaving out of account the probable discoveries in the

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subject made by Adam and Eve in the Garden of Eden, it is certain that the philosophers and alchemists were as much interested in those phenomena which lie on the border-line between physics and chemistry as in those which were purely physical or chemical. Indeed, the sharp line between the two subjects, drawn with so much emphasis twenty or thirty years ago, did not then exist. It is interesting to note that this sharp line is now rapidly being erased; we are realizing more and more that the laws which govern one class of phenomena are applicable also to the other. Thus the cosmic working of the mind of man swings back and forth; will it ever come to rest upon the absolute truth?

In the middle of the seventeenth century, while this country was in an infantile condition, and Harvard College was little more than embryonic, Robert Boyle discovered his law relating to the contraction of gases under pressure—one of our most fundamental conceptions to-day. Lavoisier, before his tragic death in the Reign of Terror, forced upon a somewhat reluctant world the idea of the conservation of mass—an idea which perhaps had been half assumed by some before—and in so doing laid a corner-stone of the great structure which was to follow. Only a few years later, Dalton, Avogadro, Ampère, Gay-Lussac, Dulong and Petit, Davy and Faraday, that prince of pioneers, with others less famous, made great additions to the world's thought in a physico-chemical direction. As far back as our forties Julius Robert Mayer and Helmholtz had acquired a clear grasp of the conservation of energy, while the other great law of energy had been partially realized by Sadi-Carnot two decades before. Hittorf's classical research on electrolytic conductivity, and Wilhelmy's epoch-making study of the speed of a reaction, a research upon the lines laid down by Wenzel and Berthollet so much earlier, took place over forty years ago. Only a decade later Guldberg and Waage laid down, in unequivocal and comprehensive terms, the fundamental law of mass-action, which is the basis of Wenzel's, Berthollet's and Wilhelmy's observations, as well as of the progress and equilibrium of every other chemical change.

Why, then, with these foundations laid so far in the past, are we inclined to call physical chemistry a brand-new structure?

We all know that a part at least of the retarded development was due to the difficulty of dealing with solutions, which seemed anomalous in so many ways. Van't Hoff, by showing that a substance in solution followed many of the laws which would govern it in the aëriform state, and Arrhenius, by explaining, in a simple way, the differences between solutions conducting electricity and those which are non-conductors, cleared the track of these obstructions; hence, for the last ten years the pace has been rapid. But it seems to me that there is another reason for the tardiness of the recognition of the importance of physical chemistry to be found in an unfortunate tendency observable sometimes in both chemists and physicists, a tendency which I am afraid we must call prejudice. Not only have untenable theories been held long after their time, but whole fields of study have been neglected by most chemists and physicists, because they lie on the border-line between the two sciences.

The average physicist only half realized that one of the most important relations of his great new force, electricity, is chemical, while the chemist does not always realize, even to this day, that Wheatstone's bridge and the telephone are chemical tools just as legitimate as, and no more 'physical' than the thermometer, or the time-honored balance, which extricated his predecessors from so hopeless a slough a hundred years ago. The day is fast approaching, however, when

both chemist and physicist will welcome every mode of acquiring more light upon the absorbing topic which engages them in common—the study of the ultimate laws and structure of the universe.

It is a pleasure to think that one of the foremost of the brilliant men who have joined in advancing this wished-for end—this union of the resources of physics and chemistry to a common purpose—since the last meeting of the American Association has had his services recognized and his opportunity enlarged by his own University of Leipzig. Wilhelm Ostwald's new laboratory for physico-chemical research is the second important university building for this purpose which has been erected in Germany, the first having been built at Göttingen for the brilliant Walther Nernst; and the fact that Ostwald should at last have obtained a material outfit worthy of his unusual mental equipment is welcomed with enthusiasm by his many warm friends. We all know what a profound effect Ostwald's surprising book, his timely Zeitschrift, and in general his broad and progressive point of view, have had upon the development of both chemistry and physics, and it has been a matter of some surprise to many that so great an influence should have emanated from a laboratory so insignificant as the old Zweitem Laboratorium, so called. The new building, although not very large, is in many respects a model; the architect and director of any kind of scientific workshop could not fail to obtain valuable hints from the detailed statement of it contained in the recently published appendix to the Zeitschrift für physikalische Chemie. What a pity that America should allow Germany to outstrip us so far in devotion to the ideals of pure science! How long will it be before we build laboratories especially for physical chemistry, or even in many colleges allot a considerable share of old buildings to this end? And yet this physical chemistry now comprehends all of the field of theoretical chemistry, except a certain kind of reasoning concerned with the structure of organic substances, and the purely chemical part of the mysterious classification called the periodic system of the elements.

Very few of the processes of nature are simple in their proximate causes or their outward manifestations, however simple the grand underlying principles may be in their ultimate essence. The old maxim, by which theories were so often consciously or unconsciously judged, 'Our theory is so simple that it must be true,' is a dangerous guide. Geber's old notion that the whole world consists of sulphur and mercury, and the topsy-turvy delusion of phlogiston, relied largely on this maxim for support, and it behooves us to avoid similar mistakes. When the ancient idea of luck had been eliminated from scientific reasonings mankind admitted that every phenomenon is a function of its controlling causes; but that all the mathematical relations should be capable of solution, although to be sure only with the aid of the potent modern methods, is a new conception. In the old days problems in chemistry which could not be solved by simple arithmetic, or at best by elementary algebra, were considered incapable of quantitative solution; now, the higher mathematics is a facile tool in the hands of many an eager chemist. Even that mystery of mysteries, the smallness of the yield in the preparation of organic substances, has a flood of light shed upon it by the phase-rule and the mass-law!

No one who is familiar with the facts can doubt that the mathematical point of view will prove in the future more and more useful to chemists, as well as to the new physical botanists and zoologists, who are bringing it to bear on their transcendently recondite problems. These last-named investigators will follow in the footsteps of

chemists, as chemists have followed in the footsteps of physicists.

The advance of the mathematical point of view in chemistry has brought with it an entirely new danger, as well as a new field of power. The accuracy of a result, of course, depends upon the accuracy of the foundation upon which the reasoning rests; and accurate mathematical processes may lead to wholly erroneous conclusions if they are based upon incomplete data. In chemistry this cause of error is especially prominent, because of the great complexity of most of the phenomena and the fact that they are often modified by subordinate influences. For this reason a physicist, used to simple phenomena and less complex effects, is especially apt, when he deals with problems allied to chemistry, to erect a large superstructure of mathematical reasoning possessing the semblance of reality upon a paper foundation, and be drearily awakened some fine day by the collapse of his air castle. The only mode of guarding against this subtle cause of disaster is to bring as much skill into every step of the experimentation as into the pure reasoning based upon the supposed facts. Here the physicist is seriously hampered by his lack of knowledge of chemistry, as well as by his usual repugnance to dealing with glass vessels and liquids; while, on the other hand, the chemist is equally hampered by his inbred dislike of brass instruments and his imperfect acquaintance with the manipulation of his new sensitive tools.

In short, one must be an accomplished chemist, physicist and mathematician in in order to attain the highest results in modern theoretical chemistry, and the number of men who have the time or ability to acquire this threefold education can never be large. All honor to van't Hoff, Ostwald, Nernst and the others who come nearest the high ideal! While it is true, however, that few men can hope to attain the highest, it does not follow that the rest of us cannot be of great use. Each man can be of value in his own particular sphere; it is only necessary that he should work faithfully with a single eye to the truth, that he should be as free as possible from prejudice, and that his published work should be as accurate as he can make it. A well conducted organic synthesis, a few carefully determined solubilities, will in the end be more valuable to the progress of science than a false generalization, no matter how ingenious the latter may be. But how great is the responsibility of the collector of facts! for if his observations are false his work is of less value even than that of the false theorist; it has not even ingenuity in its favor, and is worse than useless. Ostwald has more than once pointed to the responsibility attending publication, and we should all do well to heed his warning.

A comprehensive design which I had once harbored of giving you a *résumé* of the year's work in physico-chemical research throughout the world has been relinquished because of the great number of small papers which could not be treated satisfactorily in the brief space of an evening's talk. The subject of stoichiometry, in Ostwald's rather comprehensive interpretation of this word, has received this year the attention usually accorded to it. Solutions have still occupied many able men, without having by any means had their possibilities exhausted. Van't Hoff's admirable little book upon double salts has already begun to exercise an effect upon the chemical world which the scattered and less illuminating papers of his students could not have been expected to exercise. Dr. Gibbs' interesting address upon this important topic will undoubtedly excite further study on the whole question of the so-called 'molecular compounds,' which are so little understood and so hard to reconcile with our only partially satisfactory ideas of quantivalence. The

far-reaching subject of chemical equilibrium is receiving more and more attention every year. There has been great activity in the fascinating field of electrochemistry, and it is pleasing to see that some of the fundamental notions of this new science are coming to be recognized by the analyst and the technical chemist. Not least among the startling events of the year had been the supposed discovery of a number of new elements, crypton, neon, metargon, coronium and etherion ; if these really exist, we have here a series of brilliant chemical discoveries made solely by means of physical instruments and operations.

The most important of these interesting investigations are undoubtedly as well known to you as to your speaker, for in this day the sources of information are equally open to all; hence it would be a work of supererogation for me to discourse upon them in detail, even if there were time to do so. I prefer, therefore, to call your attention to some unpublished work with which you can hardly be so familiar ; I mean the physio-chemical problems which have enlivened the last winter's laboratory work at Harvard. Since these covered a somewhat extensive field their exposition may serve the double purpose of illustration and information. It is a pleasure to state that most of these researches would not have been thought of without the inspiring example and precept of the great men of whom I have spoken. The host of interesting investigations thus prompted in all civilized lands afford the best possible proof of the value of the modern physico-chemical hypotheses.

Dr. Gordon, the Harvard assistant in physical chemistry, has finished a very interesting series of measurements of the potentials of galvanic cells composed of metallic plates immersed in fused salts at high temperatures. After overcoming experimental difficulties, too numerous to mention, he succeeded in obtaining constant values which agree remarkably with Nernst's formula and throw interesting light on the degree of dissociation existing in fused salts.

Mr. Edward Collins has nearly finished an elaborate attempt to verify Faraday's law with rigid exactness, an attempt which has met with greater success than any previous one.

Mr. G. N. Lewis made a series of careful measurements of the change of the potential of numerous reversible electrodes with the temperature, as well as a comprehensive revision of Meyer's inaccurate work on concentration cells involving amalgams of different strengths. In the thermodynamic discussion of the results Mr. Lewis arrived at some very interesting conclusions concerning strong as well as weak solutions of metal in mercury, and extended his experiment and mathematical analysis to the consideration of the potential of the unamalgamated metal in a solution of one of its salts. It is needless to say that this question is one of wide significance, but lack of time prevents my doing more than call attention to it now. Mr. Lewis's preliminary paper will appear early in the fall.

Mr. F. R. Fraprie spent much time in studying the eccentricities of inversion temperatures and transition intervals exhibited by the double sulphates of potassium and manganese. This problem proved to be far more complex and interesting than the similar case involving magnesium instead of manganese, a case which has been so carefully investigated under Van't Hoff's supervision. While Mr. Fraprie was not able to push the matter to completion he obtained data enough to enable one to plot many of the most essential curves and to draw a mental sketch of the situation. It is hoped that this work may be continued during the present year.

Mr. Faber, in the course of a research having a more practical end as its chief

aim, made a series of determinations of the solubilities of argentic halides in solutions of sodic thiosulphate, and obtained data which may be of use in determining the mechanism of this reaction. Messrs. Harrington and Henderson made a few interesting observations on some cases in which the dissolving of a solid in a solution caused a lowering instead of a rise in the boiling point, and Mr. Churchill made a careful determination of the melting point of crystallized Glauber's salt. The aim of this last labor was to secure a new fixed point for the standardizing of thermometers, and we succeeded in showing that the point was as easily obtained and as constant at 32.484° as could be desired. This means of verifying thermometers will be a great boon to those who have not a standard instrument at hand. The paper will appear in the September numbers of the *Zeitschrift für physikalische Chemie* and the *American Journal of Science.*

Besides these varied researches, a protracted study of the causes of the occlusion, and the unequal release of gases by the oxides of metals formed from the nitrates, occupied most of my spare time. It became evident that the excess of oxygen usually present in such material has a tendency to work its way out by a process of dissociation and recombination which reminds one of the old-fashioned explanation of electrolysis. The nitrogen, not being able to escape in this fashion, is retained. This paper has just appeared in the Proceedings of the American Academy.

In addition to these, several other researches were also in progress, which, although they belong strictly to the domain of inorganic chemistry, would never have been undertaken but for the theoretical interests involved. Prominent among these were the revisions of the atomic weights of cobalt, nickel, uranium, strontium and calcium, undertaken by Dr. Cushman, Messrs. Baxter and Merigold, and myself.

Of course, it sometimes happens that physico-chemical problems involving the use of complicated apparatus may be more readily solved in a physical than in a chemical laboratory, and in any case the cooperation of these two departments is highly advisable. I am happy to say that Dr. Duane and others have been conducting such chemico-physical investigations at the Jefferson Physical Laboratory of Harvard College, but of these I have no authority to speak.

When one has been discussing the past and present progress of any subject it is natural that the mind should turn to the future also. What fields are likely to prove the most fruitful in the years to come? What researches will probably best advance the interests of science and, therefore, of the life of man? Prophecy is always an uncertain business, but if one recognizes the uncertainty it has few dangers and becomes at least amusing. In this case, however, it presents few difficulties.

The whole field of physical chemistry is so fruitful when treated by modern methods that one can hardly single out any section as especially unpromising. Almost every subject is worthy of research; a more important question is the *spirit* in which the research is to be undertaken.

There have always been two parties as regards any question brought forward by mankind for discussion—the conservative party and the radical party. The former has a tendency to cling to old ideas simply because they are old, and the latter has a tendency to adopt new ideas simply because they are new. It seems to me that neither of these tendencies is legitimate. One should seek new points of view continually, but he should hold to that which is good until something is proposed which seems to him better. In every case he should weigh the respective arguments for and against

the new point of view with a mind as free as possible from prejudice, and with a single eye to the truth. In short, the ideal investigator is the scientific independent, the chemical 'mugwump.' It is too unreasonable to hope that the problems of the twentieth century will be dealt with in this thoughtful but untrammeled fashion?

We Americans rejoice in having on our side of the ocean the world-renowned names of several great men, of Wolcott and Willard Gibbs, of James Crafts, Edward Morley, the late Josiah Parsons Cooke and others, who have combined chemistry with physics and mathematics; but, nevertheless, one must admit that America has not done as much as one could wish toward building up the fabric of modern physical chemistry. Although science is world-wide, and scientific men should be cosmopolitan, the existence of this Association proves that there is a patriotic side to the matter too. While welcoming the truth, wherever it is discovered, let us then do all we can to further its emanation from American laboratories and writing desks.

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*A CENTURY OF PERSONAL EQUATIONS.**

IN 1795 Maskelyne, Astronomer Royal at Greenwich, discovered that his assistant, Kinnebrook, was in the habit of noting star transits about seven-tenths of a second of time later than himself, and discharged the poor fellow as 'vitious' in his method of observing. The matter attracted little attention until, about twenty-five years later, the celebrated Bessel investigated it, and showed that the best observers whom he could influence exhibited similar discrepancies in their transits. Bessel himself was exceptionally early in his times, and found that other astronomers were usually later. The theory which he formed was that the early observers, Maskelyne and Bessel himself, heard their clock beats before they saw the stars' images, while the late observers, Kinnebrook, Argelander, W. Struve and others, saw first and then heard. The theory of Bessel has been generally adopted by astronomers and psychologists, and the investigation of the differences between astronomers has been pursued pretty continuously since 1836, when Airy, as Astronomer Royal at Greenwich, began a regular continuance of Bessel's investigation soon after entering upon that office. The matter was more or less perplexing to the Greenwich observers for the twenty years between 1836 and 1855. In 1853 the so-called eye-and-ear method, which had been employed for about a century previously, was laid aside at Greenwich for most purposes, and replaced by the American, or chronographic, method of galvanic registration, invented by Sears Cook Walker in 1849.

During the first half of the century, 1795 to 1895, to which this paper refers, observations of transits were made by Bradley's method, or by eye and ear, but for the second half century observers have had the benefit of Walker's invention, and of the ingenious apparatus constructed by the Bonds and other mechanicians for the purpose of carrying out the principle introduced by Walker. The investigations of personal equation up to 1853 are based, then, upon experimental psychology as developed by Bessel, and have led to a pretty complete body of empirical facts in that direction. But Bessel and his associates considered the whole matter enigmatical and difficult to trace, owing to the fact that the phenomena are subconscious and not easy to bring under the laws of experimental science. Observers noted large differences in their times, a second or more, and could not reduce them to moderate

* See also my article in SCIENCE for Nov. 26, 1897.